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Electrochemistry of Ferrocene in Acetonitrile. Evidence for
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by

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ELECTROCHEMISTRY OF FERROCENE IN ACETONITRILE EVIDENCE FOR IRREVERSIBLE KINETIC BEHAVIOR DUE TO PASSIVE FILM FORMATION

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Montenegro and Pletcher [1] have recently pointed out that measurement of the heterogeneous electron transfer rate constant of the ferrocene/ferrocenium couple at ultramicroelectrodes in acetonitrile solutions gives values that are several orders of magnitude larger than those measured at conventional electrodes. In addition, Bond et al. [2] have pointed out that there is ambiguity in the interpretation of the electrochemical behavior of this couple in organic solvents. This couple has been the subject of a large literature due to its apparent very fast rate constant in some solvents; unfortunately a wide range of values have been reported [1-10]. Bond tabulates values in aprotic solvents from 1.9×10^{-3} to 1.1 cm s^{-2} from those references; indeed, there are large discrepancies between the results from different workers on similar electrolyte/solvent systems which serves to show the difficulty in making reliable measurements on this supposedly ideal electrochemical system. The situation is further confused since it has been proposed as a potential standard couple for non-aqueous electrochemical calibration [11-16]. In his work on similar measurements on ferrocene/ferrocenium in acetonitrile at an ultramicroelectrode, Bond has discussed in detail several possible reasons for these discrepancies; they include:

- (1) Instrumental artifacts related to ohmic loss problems.
- (2) Double layer effects.
- (3) Breakdown of conventional transport theory at ultramicroelectrodes.
- (4) Weak reactant adsorption.

There is, however, little real evidence to support these possibilities.

We report here the results of simple polarization and spectroscopic experiments that indicate that the electrode is rapidly covered with a passivating layer of insoluble ferrocene complex, salt, or polymeric layer, and that the heterogeneous transfer process is therefore poorly defined in these experimental conditions.

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To a first approximation, depending on electrode preparation and for only a low number of subsequent voltammetric sweeps, the voltammetry appears to be at best a textbook case of a quasi-reversible system as suggested by the work of Kadish et al. [3]. Cyclic voltammetry at a conventional platinum electrode for a typical ferrocene system is shown in Fig. 1. The first voltammogram is at an electrode that has been cleaned in nitric + sulfuric acid, rinsed, and dried in an oven before use. The voltammogram shows a peak separation much greater than the 59 mV expected for a simple reversible one electron transfer reaction. (The voltammetry of an identical solution containing tetracyanoquinodimethane as the substrate under identical conditions indeed exhibits classical reversible one electron behavior; we have found little electrochemical or spectroelectrochemical evidence that this should not be so for that system.) Without removing the electrode from the solution, the electrode is now allowed to relax for a few minutes to allow the concentration profiles to relax to constant values. The voltammetry is then repeated, and there is a degradation in the magnitude of the anodic peak current and a positive shift in the peak potential, while the cathodic peak current falls and shifts to more negative potentials by several hundred in V (Fig. 1a). A well defined "isosbestic" point is indicated at +30 mV. After many scans (always resting to allow the current to fall to zero at the negative limit) the voltammetry relaxes to that in Fig. 1b. It is clear that the electron transfer is now ohmically controlled (above +0.1 V), and the voltammetry below +0.1 V takes on the characteristic properties of polymer film polarization electrochemistry (ca. polypyrrole film chemistry); we note the capacitive behavior of the film at negative potentials.

The electrode during the course of the experiment takes on an increasingly darker green appearance. This film is quite adherent, and may be discharged cathodically at potentials more negative than about -2.4 V, with subsequent regeneration of the voltammetry observed in the first sweep described above.

The conclusions are corroborated by measurements at an ultramicroelectrode. At a 1.0 μm diameter ultramicroelectrode in a dilute (0.1 mM) ferrocene solution (Fig. 2a), the oxidation wave is characteristic of a very fast electron transfer reaction ($> 2 \text{ cm s}^{-1}$). The mass transport of ferrocene to the surface and ferrocenium from the surface is extremely fast. At a larger (25 μm diameter) platinum ultramicroelectrode, the behavior is similar, except for the capacitive behavior which is responsible in the hysteresis on the negative sweep (Fig. 2b). At 10 times the concentration at the larger electrode, the behavior is similar, with increased capacitive contribution (Fig. 2c). At 10.0 mM ferrocene concentration, the ferrocene in reacting with another solution species, has produced enough insoluble material that it competes with the diffusing ferrocene for sites at the electrode surface; the surface is almost fully covered and passivated. The new species is nucleating the surface and the film growth process is inhibited by the rapid mass transport of ferrocenium from the surface (Fig. 2d). A characteristic feature of this behavior is that the limiting current is not a linear function of the concentration, but becomes proportionately similar as the concentration is increased. At still higher concentrations (Fig. 2e), the film growth has overcome the mass transport interference, and a passivating film covers



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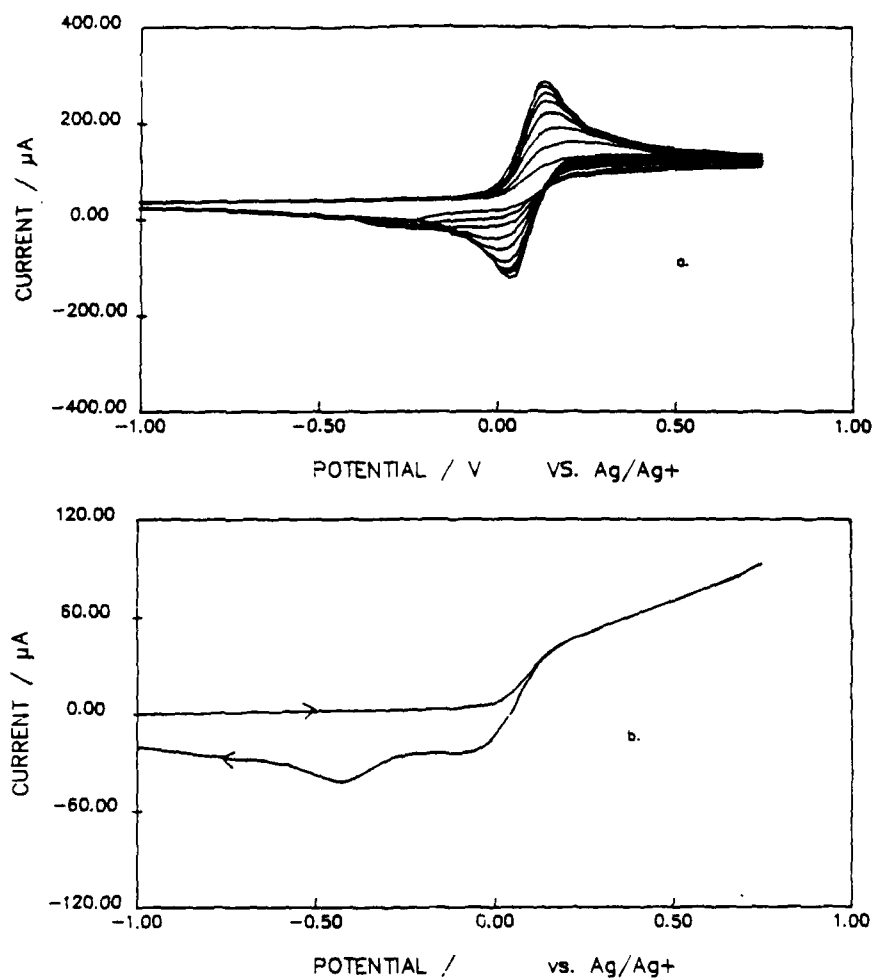


Fig. 1. (a) Cyclic voltammetry for a 10.0 mM solution of ferrocene and 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile at a platinum wire electrode, 0.01 cm^2 area. Potential scan rate was 50 mV/s. Outermost voltammogram was first scan; each successive scan was made 2 min after the preceding and is progressively smaller in magnitude. All potentials are with respect to an Ag/Ag^+ (0.01 M silver nitrate in the same electrolyte). (b) Same as above, 20th scan.

the electrode. The oxidation potential shifts dramatically in the positive direction, and the charge transfer to ferrocene occurs only at potentials high enough to cause forced migration through the film, coupled with slow diffusion through the film. We point out that these results were made under different conditions from those of the

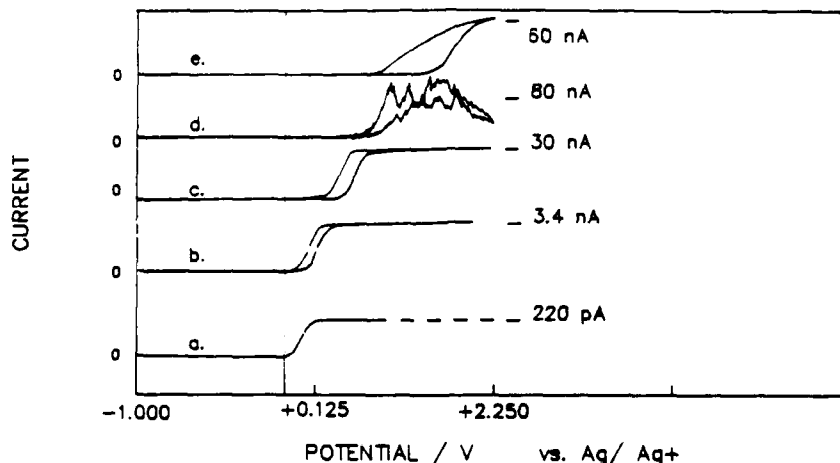


Fig. 2. (a) Voltammetry for the same solution as in Fig. 1a, except at a $1.0\ \mu\text{m}$ diameter platinum disk ultramicroelectrode, and $0.1\ \text{mM}$ ferrocene. (b) Same as Fig. 2a except at a $25\ \mu\text{m}$ diameter platinum disk ultramicroelectrode. (c) Same as Fig. 2b except in $1.0\ \text{mM}$ ferrocene. (d) Same as Fig. 2b except in $10.0\ \text{mM}$ ferrocene. (e) Same as Fig. 2b except in $50.0\ \text{mM}$ ferrocene.

Fleischmann group [17] and Murray group [18] since they were working in solvents of very high resistivity and low dielectric permittivity. The nature of the structure of the film, and the reasons for spontaneous optical emission from this film which we have also observed, is being investigated by surface infrared and optical emission spectroscopies. Preliminary infrared spectroelectrochemical results indicate that under these conditions, the film may be a precipitated ferrocenium salt.

We conclude that the electrochemistry of ferrocene in common acetonitrile electrolyte is far from ideal, and that the electrode preparation purity of components, and method of measurements of kinetic parameters should be carefully considered.

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